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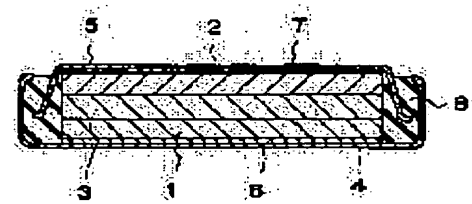
(54) LITHIUM SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a lithium secondary battery having high capacity, high energy density, low irreversible capacity, and excellent charge and discharge characteristic, even in combining with a carbon material, and high temperature.
SOLUTION: This lithium secondary battery using a carbon material as a main constituent of a negative electrode active material uses Li1−z [Mn2−x−yMxLiyO4] as a main constituent of a positive electrode active material (M is an element except Mn and Li, then (x) and (y) represent an amount of substitution of manganese, and they meet the following inequality 0<x+y≤1. Further, (z) represents an amount of reversibly usable lithium, and it meets the following inequality, −1≤z≤1).



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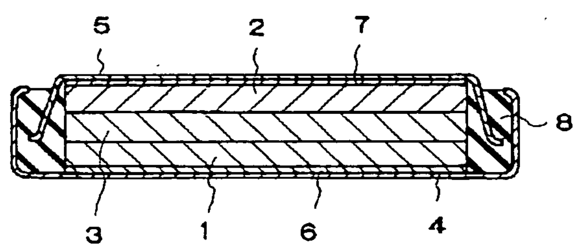
(54)【発明の名称】　リチウム二次電池

(57)【要約】

【目的】　炭素材料との組合せや高温においても高容量、高エネルギー密度で、不可逆容量の少ない充放電サイクル特性の優れたリチウム二次電池を提供することを目的とする。

【構成】　負極活物質の主構成物質として炭素材料を用いるリチウム二次電池において、正極活物質の主構成物質に$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$（ＭはＭｎとＬｉ以外の元素で、ｘ，ｙはマンガンの置換量を示し、０＜ｘ＋ｙ≦１である。また、ｚは可逆的に使用可能なリチウム量を示し、－１≦ｚ≦１である。）を用いるリチウム二次電池とすることで、上記目的を達成できる。



【特許請求の範囲】

【請求項１】　負極活物質の主構成物質として炭素材料を用いるリチウム二次電池において、正極活物質の主構成物質に$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$（ＭはＭｎとＬｉ以外の元素で、ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とするリチウム二次電池。

【請求項２】　前記正極活物質の主構成物質が、$Li_{1-z}[Mn_{2-x-y}Ca_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とする請求項１記載のリチウム二次電池。

【請求項３】　前記正極活物質の主構成物質が、$Li_{1-z}[Mn_{2-x-y}Cr_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とする請求項１記載のリチウム二次電池。

【請求項４】　前記正極活物質の主構成物質が、$Li_{1-z}[Mn_{2-x-y}In_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とする請求項１記載のリチウム二次電池。

【請求項５】　前記正極活物質の主構成物質が、$Li_{1-z}[Mn_{2-x-y}Tb_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とする請求項１記載のリチウム二次電池。

【請求項６】　前記正極活物質の主構成物質が、$Li_{1-z}[Mn_{2-x-y}Mg_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることを特徴とする請求項１記載のリチウム二次電池。

【請求項７】　前記負極活物質である炭素材料が、Ｘ線回折法による面間隔（ｄ００２）が３．３５４～３．３６９Åで、Ｃ軸方向の結晶の大きさ（Ｌｃ）が２００Å以上であることを特徴とする請求項１記載のリチウム二次電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明はリチウム二次電池に係り、放電容量、出力密度が大であって、特に高温でのサイクル特性に優れた安全性の高いリチウム二次電池用正極及び負極に関する。

【０００２】

【従来の技術】現在、４Ｖを特徴とするリチウム二次電池の正極活物質として、$LiCoO_2$、$LiNiO_2$等のα－$NaFeO_2$構造を有する含リチウム酸化物、あるいは$LiMn_2O_4$等のスピネル構造を有する含リチウム酸化物等が従来より用いられている。なかでもスピネル構造を有する$LiMn_2O_4$は、低コストかつ安全性に優れた正極活物質である。一方、負極活物質としては、従来よりリチウム金属及びリチウム合金が用いられてきたが、これらの電池は、樹枝状リチウムの析出（デンドライト）による正負両極の短絡やサイクル寿命が短く、そのためその劣化分を補償すべく電池容量の３倍当量のリチウムが必要であり、エネルギー密度が低いという欠点があった。最近ではこれらの問題点を解決するため炭素材料を負極に用いる研究が活発である。この種の負極、特に黒鉛化の進んだグラファイトを用いる場合、例えば正極にマンガン酸リチウムを用いると、電池電圧がフラットなものになり、単電池使用の携帯機器に用いる場合容量面で優位性がある。しかしながら、負極グラファイトを、正極に$LiMn_2O_4$を用いて充放電サイクルを行うと、充電時のグラファイトのドープ電圧がサイクルを重ねると０Ｖ付近となり、リチウムの析出との競争反応となってしまう。そのため、サイクル劣化が大きい要因の一つとなっていた。また、このマンガン酸リチウムはその正極活物質自身のサイクル特性が優れないことから、特開平４－２３３１６１号公報や特開平５－２１０６７号公報や特開平６－１８７９９３号公報においてはスピネル構造のマンガン酸リチウムのマンガンの一部をマンガン以外の元素で置換することが報告されている。しかしながら、これらの材料においても高温で放置しておくとマンガンが電解液に溶出することから、正極の充放電容量が減少し、サイクル劣化することが分かった。

【０００３】

【発明が解決しようとする課題】前述した如く、炭素材料を負極として用いた場合、マンガン酸リチウムとの組合せによって炭素の界面抵抗の増加という問題がある。また、正極活物質自身高温での充放電によって充放電容量が低下するという問題もある。本発明は、この問題点を解決するため、正極活物質における主構成物質に、$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$（ｘ，ｙはマンガンの置換量を示し、$0<x+y\leqq 1$である。また、ｚは可逆的に使用可能なリチウム量を示し、$-1\leqq z\leqq 1$である。）を用いることにより、炭素材料との組合せや高温においても高容量、高エネルギー密度で、不可逆容量の少ない充放電サイクル特性の優れたリチウム二次電池を提供することを目的とする。

【０００４】

【課題を解決するための手段】負極活物質として炭素を考えた場合、炭素材料へのリチウムの吸蔵、放出（インターカレーション、デインターカレーション）が主に起

こる反応だが、その反応を支配する因子の一つとして、電解液と炭素表面の間に生じる被膜状態が関与していることがわかった。例えば、リチウム金属を負極活物質にした場合で代表されるように、緻密でイオン導伝性の高い被膜はその電池特性も優れており、逆に厚くイオン伝導性の低い被膜はレート特性や、サイクル特性が悪いことが知られている。その場合、前者は炭酸リチウムや酸化リチウム等の被膜であり、後者はフッ化リチウム等の被膜であることが報告されている。これと同じことが炭素表面に生じる被膜についても考えられる。つまり、炭素材料の界面抵抗を増大させる要因の一つとして、炭素材料の表面にフッ化リチウム等のイオン伝導度の低い被膜の形成があげられる。このフッ化リチウムの被膜が形成される過程において、正極材料等から持ち込まれた水により電解質が分解して生成するフッ酸が関与していることが考えられる。本発明者らは、この問題点を解決するため種々検討した結果、スピネル構造を有するマンガン酸リチウムにおいて、マンガンの一部をリチウムと、カルシウム、クロム、インジウム、テルビウム、マグネシウム等のマンガン以外の元素で置換することにより、電池内部で生成するフッ酸を抑制することができることを見い出した。また、この正極材料は高温保存による電解液へのマンガンの溶出も抑制することが分かった。

【０００５】正極活物質の主構成物質である$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$において、ＭはＭｎとＬｉ以外の元素で、Ｍｎと置換しうる元素が好ましい。例えば、Ｂｅ，Ｂ，Ｃ，Ｓｉ，Ｐ，Ｓｃ，Ｃｕ，Ｚｎ，Ｇａ，Ｇｅ，Ａｓ，Ｓｅ，Ｓｒ，Ｍｏ，Ｐｄ，Ａｇ，Ｃｄ，Ｉｎ，Ｓｎ，Ｓｂ，Ｔｅ，Ｂａ，Ｔａ，Ｗ．Ｐｂ，Ｂｉ，Ｃｏ，Ｆｅ，Ｃｒ，Ｎｉ，Ｔｉ，Ｚｒ，Ｎｂ，Ｙ，Ａｌ，Ｎａ，Ｋ，Ｍｇ，Ｃａ，Ｃｓ，Ｌａ，Ｃｅ，Ｎｄ，Ｓｍ，Ｅｕ，Ｔｂ等が挙げられる。これらの中でもＣｒ、Ｃａ、Ｉｎ，Ｔｂ，Ｍｇはその効果が顕著であったため最も好ましい。ここで、Ｍｎの置換量を示すｘ，ｙは、$0<x+y\leqq 1$である。ただし、Ｍｎの置換量ｘ＋ｙを増やすと、可逆的に使用可能なリチウム量を示すｚが減少するため、$0<x+y\leqq 0.2$の範囲で置換することが好まし。可逆的に使用可能なリチウム量を示すｚは、Ｍｎの置換量によっても異なってくるが$-1\leqq z\leqq 1$である。

【０００６】正極活物質の主構成物質である$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$において、Ｍｎの一部をリチウムや異種元素で置換する場合、焼成原料にあらかじめ置換する元素を添加する方法や、$LiMn_2O_4$を焼成した後にイオン交換等により異種元素を置換する方法等が挙げられるが、これらに限定されるものではない。

【０００７】負極活物質に用いる炭素材料は、リチウムを吸蔵、放出可能な炭素材料であればよく、特にＸ線回折法による面間隔（ｄ００２）が３．３５４～３．３６９Åで、Ｃ軸方向の結晶の大きさ（Ｌｃ）が２００Å以上である炭素粒子は、高容量が得られるため好ましい。

【０００８】本発明に用いる正極、負極活物質は、平均粒子サイズ１００μｍ以下であることが望ましい。所定の形状を得る上で、粉体を得るためには粉砕機や分級機が用いられる。例えば、乳鉢、ボールミル、サンドミル、振動ボールミル、遊星ボールミル、ジェットミル、カウンタージェットミル、旋回気流型ジェットミル、熱プラズマや篩等が用いられる。粉砕時には水、あるいはヘキサン等の有機溶剤を共存させた湿式粉砕を用いることもできる。分級方法としては、特に限定はなく、篩や風力分級機などが乾式、湿式ともに必要に応じて用いられる。

【０００９】本発明に併せて用いることができる負極材料としては、リチウム金属、リチウム合金などや、カルコゲン化合物、メチルリチウム等のリチウムを含有する有機化合物等が挙げられる。また、リチウム金属やリチウム合金、リチウムを含有する有機化合物を併用することによって、本発明に用いる炭素材料にあらかじめリチウムを挿入することも可能である。

【００１０】本発明の正極、負極活物質を用いる場合、電極合剤として導電剤や結着剤やフィラー等を添加することができる。導電剤としては、電池性能に悪影響を及ぼさない電子伝導性材料であれば何でも良い。通常、天然黒鉛（鱗状黒鉛、鱗片状黒鉛、土状黒鉛など）、人造黒鉛、カーボンブラック、アセチレンブラック、ケッチェンブラック、カーボンウイスカー、炭素繊維や金属（銅、ニッケル、アルミニウム、銀、金など）粉、金属繊維、導電性セラミックス材料等の導電性材料を１種またはそれらの混合物として含ませることができる。これらの中で、アセチレンブラックとケッチェンブラックの併用が望ましい。その添加量は１～５０重量％が好ましく、特に２～３０重量％が好ましい。

【００１１】本発明の正極、負極活物質を用いる場合、その粉体の少なくとも表面層部分を主活物質以外のもので修飾することも可能である。例えば、金、銀、カーボン、ニッケル、銅等の電子伝導性のよい物質や、炭酸リチウム、ホウ素ガラス、固体電解質等のイオン伝導性のよい物質をメッキ、焼結、メカノフュージョン、蒸着等の技術を応用してコートすることが挙げられる。

【００１２】結着剤としては、通常、テトラフルオロエチレン、ポリフッ化ビニリデン、ポリエチレン、ポリプロピレン、エチレン－プロピレンジエンターポリマー（ＥＰＤＭ）、スルホン化ＥＰＤＭ、スチレンブタジエンゴム（ＳＢＲ）、フッ素ゴム、カルボキシメチルセルロース等といった熱可塑性樹脂、ゴム弾性を有するポリマー、多糖類等を１種または２種以上の混合物として用いることができる。また、多糖類の様にリチウムと反応する官能基を有する結着剤は、例えばメチル化するなどしてその官能基を失活させておくことが望ましい。その

添加量としては、１～５０重量％が好ましく、特に２～３０重量％が好ましい。

【００１３】フィラーとしては、電池性能に悪影響を及ぼさない材料であれば何でも良い。通常、ポリプロピレン、ポリエチレン等のオレフィン系ポリマー、アエロジル、ゼオライト、ガラス、炭素等が用いられる。フィラーの添加量は０～３０重量％が好ましい。

【００１４】電極活物質の集電体としては、構成された電池において悪影響を及ぼさない電子伝導体であれば何でもよい。例えば、正極用集電体としては、アルミニウム、チタン、ステンレス鋼、ニッケル、焼成炭素、導電性高分子、導電性ガラス等の他に、接着性、導電性、耐酸化性向上の目的で、アルミニウムや銅等の表面をカーボン、ニッケル、チタンや銀等で処理したものを用いることができる。負極用集電体としては、銅、ステンレス鋼、ニッケル、アルミニウム、チタン、焼成炭素、導電性高分子、導電性ガラス、Ａｌ－Ｃｄ合金等の他に、接着性、導電性、耐酸化性向上の目的で、銅等の表面をカーボン、ニッケル、チタンや銀等で処理したものを用いることができる。これらの材料については表面を酸化処理することも可能である。これらの形状については、フォイル状の他、フィルム状、シート状、ネット状、パンチ又はエキスパンドされたもの、ラス体、多孔質体、発泡体、繊維群の形成体等が用いられる。厚みは特に限定はないが、１～５００μｍのものが用いられる。

【００１５】正極活物質の主構成物質に$Li_{1-z}[Mn_{2-x-y}M_xLi_yO_4]$を用いる場合、他の正極活物質を添加することも可能である。例えばMnO_2，MoO_3，V_2O_5，Li_xCoO_2，Li_xNiO_2等の金属酸化物や、TiS_2，MoS_2，$NbSe_3$等の金属カルコゲン化物、ポリアセン、ポリパラフェニレン、ポリピロール、ポリアニリン、ジスルフィド等のグラファイト層間化合物、及び導電性高分子等のアルカリ金属イオンや、アニオンを吸放出可能な各種の物質を利用することができる。添加方法としては、単に混合する以外に、電解重合、メッキ、焼結、メカノフュージョン、蒸着等の技術を応用してコートすることが挙げられる。

【００１６】また、電解質としては、例えば有機電解液、高分子固体電解質、無機固体電解質、溶融塩等を用いることができ、この中でも有機電解液を用いることが好ましい。この有機電解液の有機溶媒として、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、ジエチルカーボネート、ジメチルカーボネート、メチルエチルカーボネート、γ－ブチロラクトン等のエステル類や、テトラヒドロフラン、２－メチルテトラヒドロフラン等の置換テトラヒドロフラン、ジオキソラン、ジエチルエーテル、ジメトキシエタン、ジエトキシエタン、メトキシエトキシエタン等のエーテル類、ジメチルスルホキシド、スルホラン、メチルスルホラン、アセトニトリル、ギ酸メチル、酢酸メチル、Ｎ－メチルピロリドン、ジメチルフォルムアミド等が挙げられ、これらを単独又は混合溶媒として用いることができる。また、支持電解質塩としては、$LiClO_4$、$LiPF_6$、$LiBF_4$、$LiAsF_6$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$、$LiN(C_2F_5SO_2)_2$、$LiN(CF_3SO_2)(C_4F_9SO_2)_2$等が挙げられる。一方、高分子固体電解質としては、上記のような支持電解質塩をポリエチレンオキシドやその架橋体、ポリフォスファゼンやその架橋体等といったポリマーの中に溶かし込んだものを用いることができる。さらに、Li_3N，ＬｉＩ等の無機固体電解質も使用可能である。つまり、リチウムイオン導伝性の非水電解質であればよい。

【００１７】セパレータとしては、イオンの透過度が優れ、機械的強度のある絶縁性薄膜を用いることができる。耐有機溶剤性と疎水性からポリプロピレンやポリエチレンといったオレフィン系のポリマー、ガラス繊維、ポリフッ化ビニリデン、ポリテトラフルオロエチレン等からつくられたシート、微孔膜、不織布、布が用いられる。セパレータの孔径は、一般に電池に用いられる範囲のものであり、例えば０．０１～１０μｍである。また、その厚みについても同様で、一般に電池に用いられる範囲のものであり、例えば５～３００μｍである。

【００１８】充放電特性、特にサイクル特性が向上する理由として、必ずしも明確ではないが以下のように考察される。一般的に、電池内部において、電池の充放電に関与しない種々の不純物を含んでいることが多い。例えば、$LiPF_6$を電解質に用いる場合、塩そのものが不純物を持ち込んだり、電池内部や溶媒中に含まれる極微量の水と反応することでＨＦ（フッ酸）を生じることが考えられる。リチウム吸蔵の際に炭素材料表面では、電解液と炭素材料の間に炭酸リチウムのようなイオン伝導性の高い被膜を形成するが、この被膜形成時あるいは形成後にフッ酸の様な酸が存在すると、イオン伝導性の低いハロゲン化リチウムを生じる。炭素材料と電解液の界面に生じたハロゲン化リチウムは、リチウムの吸蔵放出を妨げ、その結果負極の界面抵抗を増大させ、放電容量が低減する原因の一つと考えられる。そこで、電池内部に存在するフッ酸の量を低減することにより、この問題が解決できるのではないかと考えた。つまり、このフッ酸は電解質と水との反応によって生じるものと考えているが、正極活物質であるマンガン酸リチウムが触媒的に分解を促進しているのではないかと考え、マンガンの一部をリチウムとマンガン以外の元素で置換したスピネル構造を有するマンガン酸リチウムを用いることにより、分解等に及ぼす触媒的な活性を落とし、水と電解質との分解反応によって生じるフッ酸を低減すると考た。さらに、この触媒的な活性度は、スピネル構造を有する$LiMn_2O_4$の充電末物質である$\gamma-MnO_2$が最も高く、マンガンの一部をリチウムとマンガン以外の元素で

置換することにより、このγ－MnO_2の生成を抑制し触媒活性が低減することができると考え、マンガンの一部をリチウムとマンガン以外の元素で置換したスピネル構造を有するマンガン酸リチウムを用いることで、負極の炭素材料の界面抵抗増大が抑制され、サイクル特性が向上したため、本発明に至った。また、このマンガンの一部をリチウムとマンガン以外の元素で置換したスピネル構造を有するマンガン酸リチウムは、触媒活性が低減しただけでなく、高温に於ける活物質自身の安定性も向上し、高温に於けるサイクル特性も向上することが分かった。

【００１９】

【実施例】以下、本発明を実施例に基づき説明する。

【００２０】（実施例１）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物と酢酸カルシウム一水和物とをＬｉとＭｎとＣａの比が１．１０：１．９５：０．０５になるように混合し、これを酢酸に溶解した。熱を加えながら撹拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。次にエネルギー分散型電子プローブマイクロアナリシス（ＥＰＭＡ）によりカルシウムの分散状態を観察したところ、カルシウムはマンガン酸リチウムの全面に分布していた。この粉末を粉末Ａとする。

【００２１】（実施例２）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物と酢酸クロム（ＩＩＩ）とをＬｉとＭｎとＣｒの比が１．１０：１．９５：０．０５になるように混合し、これを酢酸に溶解した。熱を加えながら撹拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。次にＥＰＭＡによりクロムの分散状態を観察したところ、クロムはマンガン酸リチウムの全面に分布していた。この粉末を粉末Ｂとする。

【００２２】（実施例３）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物と酢酸インジウム（ＩＩＩ）水和物とをＬｉとＭｎとＩｎの比が１．１０：１．９５：０．０５になるように混合し、これを酢酸に溶解した。熱を加えながら撹拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。次にＥＰＭＡによりインジウムの分散状態を観察したところ、インジウムはマンガン酸リチウムの全面に分布していた。この粉末を粉末Ｃとする。

【００２３】（実施例４）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物と酢酸テルビウム（ＩＩＩ）四水和物とをＬｉとＭｎとＴｂの比が１．１０：１．９５：０．０５になるように混合し、これを酢酸に溶解した。熱を加えながら撹拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。次にＥＰＭＡによりテルビウムの分散状態を観察したところ、テルビウムはマンガン酸リチウムの全面に分布していた。この粉末を粉末Ｄとする。

【００２４】（実施例５）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物と酢酸マグネシウム（ＩＩ）四水和物とをＬｉとＭｎとＭｇの比が１．１０：１．９５：０．０５になるように混合し、これを酢酸に溶解した。熱を加えながら撹拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。次にＥＰＭＡによりクロム元素の分散状態を観察したところ、マグネシウムはマンガン酸リチウムの全面に分布していた。この粉末を粉末Ｅとする。

【００２５】（実施例６）上記実施例１で得られた粉末Ａ，Ｂ，Ｃ，Ｄ，Ｅを正極活物質として用い、次のようにして図１に示すコイン型非水電解質電池を試作した。正極１は、粉末Ａ～粉末Ｅとアセチレンブラック及びポリテトラフルオロエチレン粉末とを重量比８５：１０：５で混合し、トルエンを加えて十分混練した。これをローラープレスにより厚み０．８ｍｍのシート状に成形した。次にこれを直径１６ｍｍの円形に打ち抜き、減圧下２００℃で１５時間乾燥し正極１を得た。正極１は正極集電体６の付いた正極缶４に圧着して用いた。負極活物質として、人造黒鉛（平均粒径６μｍ、Ｘ線回折法による面間隔（ｄ００２）が３．３７Åで、Ｃ軸方向の結晶の大きさ（Ｌｃ）が５５０Åとポリテトラフルオロエチレン粉末とを重量比９５：５で混合し、トルエンを加えて十分混練した。これをローラープレスにより厚み０．１ｍｍのシート状に成形した。次にこれを直径１６ｍｍの円形に打ち抜き、減圧下２００℃で１５時間乾燥して負極２を得た。負極２は負極集電体７の付いた負極缶５に圧着して用いた。エチレンカーボネートとジエチルカーボネートとの体積比１：１の混合溶剤に$LiPF_6$を１ｍｏｌ／ｌ溶解した電解液を用い、セパレータ３にはポリプロピレン製微多孔膜を用いた。上記正極、負極、電解液及びセパレータを用いて直径２０ｍｍ、厚さ１．６ｍｍのコイン型リチウム電池を作製した。この粉末Ａ～Ｅを用いた電池をそれぞれ電池（Ａ）～電池（Ｅ）とする。

【００２６】（比較例）酢酸リチウム二水和物と酢酸マンガン（ＩＩ）四水和物とをＬｉとＭｎの比が１．１０：２．００になるように混合し、これを酢酸に溶解した。熱を加えながら攪拌し、完全に溶解した溶液から酢酸を蒸発させ、混合塩を得た。この混合塩を５００℃で仮焼成し、空気中８５０℃で焼成した。得られた焼成物を粉砕し、このＸＲＤ測定を行った結果、スピネル構造を有するマンガン酸リチウムが得られていることが分かった。この粉末を粉末Ｃとする。粉末Ａの代わりに、粉末Ｆを用い、それ以外は実施例３と同様にして電池を作＊製した。得られた電池を比較電池（Ｆ）とする。

【００２７】これらの電池（Ａ）～（Ｅ）、及び比較電池（Ｆ）を用いて充放電試験を行なった。充電終止電圧を４．２Ｖ、放電終止電圧を３．０Ｖとし、充放電電流を１ｍＡ、試験温度は２０℃と４０℃で定電流充放電を行った。得られた５サイクル目の放電容量の結果を表１に示した。また、サイクル寿命として放電容量が初期の６０％に低下した時点のサイクル数を測定した。

【００２８】

【表１】

電　池	２０℃での放電容量（mAh）	サイクル寿命（サイクル数）	４０℃での放電容量（mAh）	サイクル寿命（サイクル数）
電池Ａ	１６	２８５	１７	１４５
電池Ｂ	１６	２６５	１７	１４０
電池Ｃ	１６	３００	１７	１６０
電池Ｄ	１６	２６５	１７	１４０
電池Ｅ	１６	２７５	１７	１４５
比較電池Ｆ	１７	８０	１４	１０

【００２９】粉末Ａ～粉末Ｅを用いた電池（Ａ）～電池（Ｅ）と比較電池（Ｆ）を比較して初期の放電容量は変わらなかったが、サイクル寿命が良くなることが分かる。また、４０℃の高温においては、初期の放電容量は増大し、サイクル寿命も向上することが分かる。つまり、本発明の正極活物質を用いることにより、電解質の分解が少なく、これによってフッ酸の生成が抑制されるため、炭素表面に生成する表面被膜において、フッ酸の存在下生成する抵抗の高いフッ化リチウムではなく、フッ素の関与しない比較的抵抗の低い炭酸リチウムや酸化リチウムといったような成分の被膜が形成され、界面抵抗増大が抑制されサイクル特性が向上することが考えられる。また、高温の４０℃でのサイクル特性も優れていることから、電解質の分解だけでなく、正極活物質自身の電解液へのマンガンの溶出も抑えられ、活物質の容量低下も抑制されることが考えられる上記実施例においては、正極活物質における主構成物質に$Li[Mn_{1.95}Ca_{0.05}Li_{0.10}O_4]$、$Li[Mn_{1.95}Cr_{0.05}Li_{0.10}O_4]$、$Li[Mn_{1.95}In_{0.05}Li_{0.10}O_4]$、$Li[Mn_{1.95}Tb_{0.05}Li_{0.10}O_4]$ $Li[Mn_{1.95}Mg_{0.05}Li_{0.10}O_4]$を、負極材料として人造黒鉛を用いたリチウム二次電池について挙げたが、同様の効果が他の置換元素及び負極材料についても確認された。なお、本発明は上記実施例に記載された活物質の出発原料、製造方法、正極、負極、電解質、セパレータ及び電池形状などに限定されるものではない。

【００３０】

【発明の効果】本発明は上述の如く構成されているので、正極活物質の主構成物質であるスピネル構造を有するマンガン酸リチウムのマンガンの一部をリチウムとマンガン以外の元素で置換することにより、負極活物質である炭素材料界面での抵抗増大が少なく、さらに正極活物質自身の熱安定性が向上しサイクル特性が向上する。また、その材料が安全性に優れ、安価であることから、正極材料の優れた改質の方法であり、その結果得られる電池は、高容量、高エネルギー密度で、高温においても優れた充放電サイクル特性を示す。

【図面の簡単な説明】

【図１】本発明の実施例に係るコイン型非水電解質電池の断面図である。

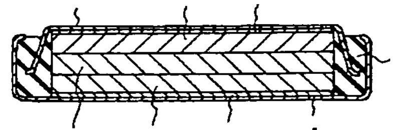
【符号の説明】

１　正極

2　負極
3　セパレータ
4　正極缶

＊5　負極缶
6　正極集電体
＊　7　負極集電体

【図1】



フロントページの続き

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

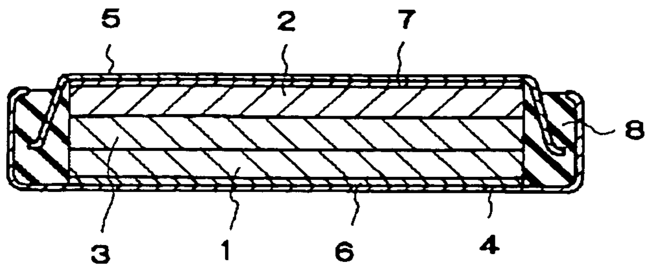
[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] It sets to the lithium secondary battery using a carbon material as a main constituent of a negative-electrode active material, and is Li1-z [Mn2-x-y Mx Liy O4] (M is elements other than Mn and Li, and x and y show the amount of substitution of manganese, and are 0<x+y<=1.) to the main constituent of a positive active material. Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery characterized by using.
[Claim 2] The main constituent of the aforementioned positive active material is Li1-z [Mn2-x-y CaxLiy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.). Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery according to claim 1 characterized by using.
[Claim 3] The main constituent of the aforementioned positive active material is Li1-z [Mn2-x-y CrxLiy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.). Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery according to claim 1 characterized by using.
[Claim 4] The main constituent of the aforementioned positive active material is Li1-z [Mn2-x-y InxLiy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.). Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery according to claim 1 characterized by using.
[Claim 5] The main constituent of the aforementioned positive active material is Li1-z [Mn2-x-y TbxLiy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.). Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery according to claim 1 characterized by using.
[Claim 6] The main constituent of the aforementioned positive active material is Li1-z [Mn2-x-y MgxLiy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.). Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. Lithium secondary battery according to claim 1 characterized by using.
[Claim 7] The lithium secondary battery according to claim 1 characterized by the size (Lc) of the crystal of the spacing (d002) according [the carbon material which is the aforementioned negative-electrode active material] to an X-ray diffraction method of C shaft orientations by 3.354-3.369A being 200A or more.

[Translation done.]

Drawing selection [Representative drawing]



[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to a lithium secondary battery, and service capacity and power density are size and it relates to the high positive electrode for lithium secondary batteries and high negative electrode of the safety which was especially excellent in the cycle property in an elevated temperature.
[0002]
[Description of the Prior Art] as the positive active material of the lithium secondary battery characterized by 4V now -- $LiCoO_2$ and $LiNiO_2$ etc. -- alpha-$NaFeO_2$ The ** lithium oxide which has structure, or $LiMn_2O_4$ etc. -- the ** lithium oxide which has Spinel structure is used conventionally $LiMn_2O_4$ which has Spinel structure especially It is the positive active material excellent in a low cost and safety. On the other hand, as a negative-electrode active material, although the lithium metal and the lithium alloy had been used conventionally, that the short circuit and cycle life of positive/negative two poles by deposit (dendrite) of an arborescence lithium are short, and a part for the degradation should be compensated for the reason, the lithium of the 3 time equivalent of cell capacity is required for these cells, and they had a fault of a low in an energy density. In order to solve these troubles recently, the research which uses a carbon material for a negative electrode is active. When using the graphite to which this kind of negative electrode, especially graphitization progressed (for example, if a manganic acid lithium is used for a positive electrode, when a cell voltage will become a flat and will use for the pocket device of cell use), it is predominant in respect of capacity. However, it is $LiMn_2O_4$ to a positive electrode about negative-electrode graphite. If it uses and a charge-and-discharge cycle is performed, if the dope voltage of the graphite at the time of charge piles up a cycle, it will become the 0V neighborhood, and will become competitive reaction with a deposit of a lithium. Therefore, cycle degradation was set to one of the large factors. Moreover, since this manganic acid lithium is not excellent in the cycle property of a positive active material own [the], replacing some manganese of the manganic acid lithium of Spinel structure by elements other than manganese in JP,4-233161,A, JP,5-21067,A, or JP,6-187993,A is reported. However, since manganese was eluted in the electrolytic solution when it was left at the elevated temperature also in such material, the charge-and-discharge capacity of a positive electrode decreased, and it turns out that cycle degradation is carried out.
[0003]
[Problem(s) to be Solved by the Invention] As mentioned above, when a carbon material is used as a negative electrode, there is a problem of the increase in a carbonaceous interfacial resistance with combination with a manganic acid lithium. Moreover, there is also a problem that charge-and-discharge capacity falls by the charge and discharge in the elevated temperature of a positive active material itself. this invention is Li_{1-z} [Mn_{2-x-y} M_x Li_y O_4] (x and y show the amount of substitution of manganese, and are $0<x+y<=1$.) to the main constituent [in / a positive active material / since this trouble is solved]. Moreover, z shows the amount of lithiums usable in reversible, and is $-1<=z<=1$. By using, also in combination with a carbon material, or an elevated temperature, it is high capacity and high-energy density, and aims at offering the lithium secondary battery which was excellent in the charge-and-discharge cycle property with little irreversible capacity.
[0004]
[Means for Solving the Problem] Although the occlusion of the lithium to a carbon material and discharge (an intercalation, day intercalation) were the reactions which mainly occur when carbon was considered as a negative-electrode active material, it turns out that the coat state produced between the electrolytic solution and a carbon front face is involving as one of the factors which govern the reaction. For example, it is precise, the high coat of ion conductivity is excellent also in the cell property, and it is known that an ion conductivity conversely thick low coat has bad rate property and cycle property so that it may be represented with the case where a lithium metal is made into a negative-electrode active material. In this case, the former is coats, such as a lithium carbonate and a lithium oxide, and it is reported that the latters are coats, such as lithium fluoride. The coat which the same thing as

this produces on a carbon front face is also considered. That is, formation of the low coat of ionic conductivity, such as lithium fluoride, is raised on the surface of a carbon material as one of the factors which increases the interfacial resistance of a carbon material. In process in which the coat of this lithium fluoride is formed, it is possible that the fluoric acid which an electrolyte decomposes with the water carried in from positive-electrode material etc., and is generated is involving. This invention persons found out that the fluoric acid generated inside a cell could be suppressed in the manganic acid lithium which has Spinel structure by replacing some manganese by elements other than manganese, such as a lithium, calcium and chromium, an indium, a terbium, and magnesium, as a result of examining many things, in order to solve this trouble. Moreover, it turns out that this positive-electrode material also suppresses elution of the manganese to the electrolytic solution by elevated-temperature preservation.

[0005] Li1-z which is the main constituent of a positive active material In [Mn2-x-y Mx Liy O4], M is elements other than Mn and Li, and its element which can be replaced by Mn is desirable. For example, Be, B, C, Si, P, Sc, Cu, Zn, Ga, germanium, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W.Pb, Bi, Co, Fe, Cr, nickel, Ti, Zr, Nb, Y, aluminum, Na, K, Mg, calcium, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. are mentioned. Also in these, since the effect of Cr, calcium, In, Tb, and Mg was remarkable, they are the most desirable. Here, x and y which show the amount of substitution of Mn are $0<x+y<=1$. however, the thing replaced in $0<x+y<=0.2$ in order that z which shows the amount of lithiums usable in reversible may decrease, if amount x+y of substitution of Mn is increased -- good -- better Although z which shows the amount of lithiums usable in reversible changes also with amounts of substitution of Mn, it is $-1<=z<=1$.

[0006] Li1-z which is the main constituent of a positive active material The method of adding the element beforehand replaced by the baking raw material in [Mn2-x-y Mx Liy O4], when a lithium and a different-species element replace a part of Mn, and LiMn 2O4 Although the way the ion exchange etc. replaces a different-species element etc. is mentioned after calcinating, it is not limited to these.

[0007] The spacing (d002) especially by the X-ray diffraction method is 3.354 to 3.369 A, and since high capacity is obtained, the carbon particle whose size (Lc) of the crystal of C shaft orientations is 200A or more is [that the carbon material used for a negative-electrode active material should just be a carbon material which emits / occlusion and / a lithium] desirable.

[0008] As for the positive electrode used for this invention, and a negative-electrode active material, it is desirable that it is 100 micrometers or less of average grain size. When acquiring a predetermined configuration, a grinder and a classifier are used in order to obtain fine particles. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, a counter jet mill, a revolution air current type jet mill, a thermal plasma, a screen, etc. are used. At the time of trituration, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification method, there is especially no limitation and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.

[0009] As a negative-electrode material which can be combined and can be used for this invention, the organic compound containing lithiums, such as a lithium metal, a lithium alloy, etc. and a chalcogen compound, a methyl lithium, etc. is mentioned. Moreover, it is also possible by using together the organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in the carbon material used for this invention beforehand.

[0010] the case where the positive electrode of this invention and a negative-electrode active material are used -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture If it is the electronic-conduction nature material which does not have a bad influence on a cell performance as an electric conduction agent, it is good anything. Usually, conductive material, such as natural graphites (a flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and a conductive ceramic material, can be included as one sort or those mixture. In these, combined use of acetylene black and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0011] When using the positive electrode of this invention, and a negative-electrode active material, the thing of the fine particles for which it is things other than the main active material, and a surface-layer portion is embellished at least is also possible. For example, applying technology, such as plating, sintering, a mechano fusion, and vacuum evaporationo, and carrying out the coat of the ion conductivity good matter, such as good matter of electronic-conduction nature, such as gold, silver, carbon, nickel, and copper, and a lithium carbonate, boron glass, a solid electrolyte, is mentioned.

[0012] As a binder, thermoplastics, such as a tetrafluoroethylene, a polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a carboxymethyl cellulose, the polymer which has rubber elasticity, polysaccharide, etc. can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to make the

functional group deactivate. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.
[0013] If it is the material which does not have a bad influence on a cell performance as a filler, it is good anything. Usually, olefin system polymer, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. The addition of a filler has 0 - 30 desirable % of the weight.
[0014] If it is the electronic-conduction object which does not do a bad influence in the constituted cell as a charge collector of an electrode active material, it is good anything. For example, as a charge collector for positive electrodes, besides aluminum, titanium, stainless steel, nickel, a baked carbon, a conductive polymer, electrically conductive glass, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As a charge collector for negative electrodes, besides copper, stainless steel, nickel, aluminum, titanium, a baked carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About such material, it is also possible to oxidize a front face. About these configurations, the shape of the shape of others and a film and a sheet, the letter of a network, punch or the thing by which expanded one was carried out, a lath object, a porosity object, a foam, the organizer of a fiber group, etc. are used. [shape / of foil] Although especially limitation is thin, a 1-500-micrometer thing is used.
[0015] It is Li1-z to the main constituent of a positive active material. When using [Mn2-x-y Mx Liy O4], it is also possible to add other positive active materials. for example, MnO2, MoO3, V2 O5, Lix CoO2, and Lix NiO2 etc. -- a metallic oxide, and TiS2, MoS2 and NbSe3 etc. -- various kinds of matter in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, the poly aniline, and disulfide, and a conductive polymer, and an anion Applying and carrying out the coat of the technology, such as electrolytic polymerization, plating, sintering, a mechano fusion, and vacuum evaporationo, as the addition method besides only mixing is mentioned.
[0016] Moreover, it is desirable to be able to use the organic electrolytic solution, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., for example, and to use the organic electrolytic solution also in this as an electrolyte. As an organic solvent of this organic electrolytic solution, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Substitution tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, A dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, a dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO4, LiPF6, LiBF4, LiAsF6, LiCF3 SO3, LiN (CF3 SO2)2, LiN (C2 F5 SO2)2, and LiN (CF3 SO2) (C4 F9 SO2)2 etc. -- it is mentioned On the other hand, what melted the above supporting-electrolyte salts as a solid polymer electrolyte into polymer, such as a polyethylene oxide, the bridge formation object and poly force FAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li3 N and LiI, are also usable. That is, what is necessary is just nonaqueous electrolyte of lithium ion conductivity.
[0017] As separator, the transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. The sheet built with the polymer of olefin systems, such as organic-solvent-proof nature, hydrophobic shell polypropylene, and polyethylene, the glass fiber, the polyvinylidene fluoride, the polytetrafluoroethylene, etc., a micropore film, a nonwoven fabric, and cloth are used. The aperture of separator is a thing of the range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of the range generally used for a cell, for example, is 5-300 micrometers.
[0018] As a reason a charge-and-discharge property, especially whose cycle property improve, although it is not necessarily clear, it is considered as follows. Generally, in the interior of a cell, the various impurities which do not participate in the charge and discharge of a cell are included in many cases. For example, LiPF6 When using for an electrolyte, the salt itself can carry in an impurity or it is possible to produce HF (fluoric acid) reacting with the water of the ultralow volume contained in the interior of a cell, or a solvent. Although an ion conductivity high coat like a lithium carbonate is formed between the electrolytic solution and a carbon material on a carbon-material front face in the case of lithium occlusion, if an acid like fluoric acid exists after the time of this coat formation, or formation, an ion conductivity low lithium halide will be produced. The lithium halide produced in the interface of a carbon material and the electrolytic solution bars occlusion discharge of a lithium, as a result, increases the interfacial resistance of a negative electrode, and is considered to be one of the causes which service capacity reduces. Then, I thought that this problem would be solvable by reducing the amount of the fluoric acid which exists in the interior of a cell. That is, by the manganic acid lithium which is a positive active material thinking that decomposition will be promoted in catalyst, and using the manganic acid lithium which has the Spinel structure

which replaced some manganese by elements other than a lithium and manganese, although it thinks that it is generated by the reaction of an electrolyte and water, this fluoric acid is ****, when the fluoric acid which drops the catalyst-activity exerted on decomposition etc. and is produced by the decomposition reaction of water and an electrolyte is reduced. Furthermore, this catalyst-activity is LiMn 2O4 which has Spinel structure. Gamma-MnO 2 which is the matter after charge By being the highest and replacing some manganese by elements other than a lithium and manganese This gamma-MnO 2 By using the manganic acid lithium which has the Spinel structure which suppressed generation, thought that catalytic activity could be reduced and replaced some manganese by elements other than a lithium and manganese Since interfacial-resistance increase of the carbon material of a negative electrode was suppressed and the cycle property improved, it resulted in this invention. Moreover, it turns out that its stability of an active material own [hot] improves catalytic activity not only reduced the manganic acid lithium which has the Spinel structure which replaced a part of this manganese by elements other than a lithium and manganese, but, and a hot cycle property also improves.
[0019]
[Example] Hereafter, this invention is explained based on an example.
[0020] (Example 1) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the calcium-acetate monohydrate were mixed so that Li and the ratio of Mn and calcium might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of calcium was observed by energy-dispersion type electron probe microanalysis (EPMA), calcium was distributed all over the manganic acid lithium. Let this powder be Powder A.
[0021] (Example 2) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the chromium acetate (III) were mixed so that the ratio of Li, and Mn and Cr might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of chromium was observed by EPMA, chromium was distributed all over the manganic acid lithium. Let this powder be Powder B.
[0022] (Example 3) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the acetic-acid indium (III) hydrate were mixed so that the ratio of Li, and Mn and In might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of an indium was observed by EPMA, the indium was distributed all over the manganic acid lithium. Let this powder be Powder C.
[0023] (Example 4) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and acetic-acid terbium (III) 4 hydrate were mixed so that Li and the ratio of Mn and Tb might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of a terbium was observed by EPMA, the terbium was distributed all over the manganic acid lithium. Let this powder be Powder D.
[0024] (Example 5) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and magnesium-acetate (II) 4 hydrate were mixed so that Li and the ratio of Mn and Mg might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of a chromium element was observed by EPMA, magnesium was distributed all over the manganic acid lithium. Let this powder be Powder E.
[0025] (Example 6) The coin type nonaqueous electrolyte cell shown in drawing 1 as follows was made as an experiment, using the powder A, B, C, D, and E obtained in the above-mentioned example 1 as a positive active material. The positive electrode 1 mixed Powder A - Powder E, acetylene black, and polytetrafluoroethylene powder by the weight ratio 85:10:5, added toluene, and kneaded it enough. This was fabricated with a thickness of

0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, and dried at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. As a negative-electrode active material, it is an artificial graphite (the size (Lc) of the crystal of the spacing (d002) by 6 micrometers of mean particle diameters and the X-ray diffraction method of C shaft orientations by 3.37A mixed 550A and polytetrafluoroethylene powder by the weight ratio 95:5, added toluene, and kneaded enough.). This was fabricated with a thickness of 0.1mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it dried at 200 degrees C under reduced pressure for 15 hours, and the negative electrode 2 was obtained The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached. It is LiPF6 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porous membrane made from polypropylene was used for separator 3 using the electrolytic solution which carried out 1 mol/l dissolution. The coin type lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and separator. Let the cells using this powder A-E be a cell (A) - a cell (E), respectively.

[0026] (Example of comparison) The acetic-acid lithium dihydrate and manganese acetate (II)4 hydrate were mixed so that the ratio of Li and Mn might be set to 1.10:2.00, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Let this powder be Powder C. Instead of Powder A, Powder F was used and the cell was produced like the example 3 except it. Let the obtained cell be a comparison cell (F).

[0027] These cells (A) The charge and discharge test was performed using - (E) and the comparison cell (F). Charge final voltage was set to 4.2V, the discharge final voltage was set to 3.0V, and 1mA and the test temperature performed constant-current charge and discharge for the charge and discharge current at 20 degrees C and 40 degrees C. The result of the service capacity of obtained 5 cycle eye was shown in Table 1. Moreover, the number of cycles at the time of service capacity falling to 60% of the first stage as a cycle life was measured.

[0028]

[Table 1]

電　池	２０℃での放電容量（mAh）	サイクル寿命（サイクル数）	４０℃での放電容量（mAh）	サイクル寿命（サイクル数）
電池Ａ	１６	２８５	１７	１４５
電池Ｂ	１６	２６５	１７	１４０
電池Ｃ	１６	３００	１７	１６０
電池Ｄ	１６	２６５	１７	１４０
電池Ｅ	１６	２７５	１７	１４５
比較電池Ｆ	１７	８０	１４	１０

[0029] Although the cell (A) - cell (E), and comparison cell (F) using Powder A - Powder E were compared and early service capacity did not change, a cycle life is good and a bird clapper is known. Moreover, in the elevated temperature of 40 degrees C, it turns out that early service capacity increases and a cycle life also improves. That is, there is little electrolytic disassembly by using the positive active material of this invention, and since generation of fluoric acid is suppressed by this, in the surface lining generated on a carbon front face, it is possible [it] that the coat of the component like not the high lithium fluoride of the resistance generated under existence of fluoric acid but the lithium carbonate with comparatively low resistance in which a fluorine does not participate and a lithium

oxide is formed, interfacial-resistance increase is suppressed, and a cycle property improves. moreover, since the 40-degree C hot cycle property is also excellent, not only in electrolytic disassembly In the above-mentioned example which can consider that elution of the manganese to the own electrolytic solution of a positive active material is also suppressed, and capacity deterioration of an active material is also suppressed To the main constituent in a positive active material, Li [Mn1.95calcium0.05Li 0.10O4], Li [Mn1.95Cr0.05Li 0.10O4] and Li [Mn1.95In0.05Li 0.10O4], Li [Mn1.95Tb0.05Li 0.10O4] Although Li [Mn1.95Mg0.05Li 0.10O4] was mentioned about the lithium secondary battery using the artificial graphite as a negative-electrode material, the same effect was checked about other substitution elements and negative-electrode material. In addition, this invention is not limited to the start raw material, the manufacture method, a positive electrode, a negative electrode, an electrolyte, separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.

[0030]

[Effect of the Invention] Since this invention is constituted like ****, by replacing some manganese of the manganic acid lithium which has the Spinel structure which is the main constituent of a positive active material by elements other than a lithium and manganese, it has little resistance increase by the carbon-material interface which is a negative-electrode active material, its own thermal stability of a positive active material improves further, and its cycle property improves. Moreover, it is the method of reforming which the material was excellent in safety, and was excellent in positive-electrode material since it was cheap, and the cells obtained as a result are high capacity and high-energy density, and show the charge-and-discharge cycle property of having excelled also in the elevated temperature.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to a lithium secondary battery, and service capacity and power density are size and it relates to the high positive electrode for lithium secondary batteries and high negative electrode of the safety which was especially excellent in the cycle property in an elevated temperature.
[0002]

[Translation done.]

PRIOR ART

[Description of the Prior Art] as the positive active material of the lithium secondary battery characterized by 4V now -- LiCoO2 and LiNiO2 etc. -- alpha-NaFeO 2 The ** lithium oxide which has structure, or LiMn 2O4 etc. -- the ** lithium oxide which has Spinel structure is used conventionally LiMn 2O4 which has Spinel structure especially It is the positive active material excellent in a low cost and safety. On the other hand, as a negative-electrode active material, although the lithium metal and the lithium alloy had been used conventionally, that the short circuit and cycle life of positive/negative two poles by deposit (dendrite) of an arborescence lithium are short, and a part for the degradation should be compensated for the reason, the lithium of the 3 time equivalent of cell capacity is required for these cells, and they had the fault that an energy density was low. In order to solve these troubles recently, the research which uses a carbon material for a negative electrode is active. When using the graphite to which this kind of negative electrode, especially graphitization progressed (for example, if a manganic acid lithium is used for a positive electrode, when a cell voltage will become a flat and will use for the pocket device of cell use), it is predominant in respect of capacity. However, it is LiMn 2O4 to a positive electrode about negative-electrode graphite. If it uses and a charge-and-discharge cycle is performed, if the dope voltage of the graphite at the time of charge piles up a cycle, it will become the 0V neighborhood, and will become competitive reaction with a deposit of a lithium. Therefore, cycle degradation was set to one of the large factors. Moreover, since this manganic acid lithium is not excellent in the cycle property of a positive active material own [the], replacing some manganese of the manganic acid lithium of Spinel structure by elements other than manganese in JP,4-233161,A, JP,5-21067,A, or JP,6-187993,A is reported. However, since manganese was eluted in the electrolytic solution when it was left at the elevated temperature also in such material, the charge-and-discharge capacity of a positive electrode decreased, and it turns out that cycle degradation is carried out.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] Since this invention is constituted like ****, by replacing some manganese of the manganic acid lithium which has the Spinel structure which is the main constituent of a positive active material by elements other than a lithium and manganese, it has little resistance increase by the carbon-material interface which is a negative-electrode active material, its own thermal stability of a positive active material improves further, and its cycle property improves. Moreover, it is the method of reforming which the material was excellent in safety, and was excellent in positive-electrode material since it was cheap, and the cells obtained as a result are high capacity and high-energy density, and show the charge-and-discharge cycle property of having excelled also in the elevated temperature.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] As mentioned above, when a carbon material is used as a negative electrode, there is a problem of the increase in a carbonaceous interfacial resistance with combination with a manganic acid lithium. Moreover, there is also a problem that charge-and-discharge capacity falls by the charge and discharge in the elevated temperature of a positive active material itself. this invention is Li1-z [Mn2-x-y Mx Liy O4] (x and y show the amount of substitution of manganese, and are 0<x+y<=1.) to the main constituent [in / a positive active material / since this trouble is solved]. Moreover, z shows the amount of lithiums usable in reversible, and is -1<=z<=1. By using, also in combination with a carbon material, or an elevated temperature, it is high capacity and high-energy density, and aims at offering the lithium secondary battery which was excellent in the charge-and-discharge cycle property with little irreversible capacity.

[Translation done.]

MEANS

[Means for Solving the Problem] Although the occlusion of the lithium to a carbon material and discharge (an intercalation, day intercalation) were the reactions which mainly occur when carbon was considered as a negative-electrode active material, it turns out that the coat state produced between the electrolytic solution and a carbon front face is involving as one of the factors which govern the reaction. For example, it is precise, the high coat of ion conductivity is excellent also in the cell property, and it is known that an ion conductivity conversely thick low coat has bad rate property and cycle property so that it may be represented with the case where a lithium metal is made into a negative-electrode active material. In this case, the former is coats, such as a lithium carbonate and a lithium oxide, and it is reported that the latters are coats, such as lithium fluoride. The coat which the same thing as this produces on a carbon front face is also considered. That is, formation of the low coat of ionic conductivity, such as lithium fluoride, is raised on the surface of a carbon material as one of the factors which increases the interfacial resistance of a carbon material. In process in which the coat of this lithium fluoride is formed, it is possible that the fluoric acid which an electrolyte decomposes with the water carried in from positive-electrode material etc., and is generated is involving. This invention persons found out that the fluoric acid generated inside a cell could be suppressed in the manganic acid lithium which has Spinel structure by replacing some manganese by elements other than manganese, such as a lithium, calcium and chromium, an indium, a terbium, and magnesium, as a result of examining many things, in order to solve this trouble. Moreover, it turns out that this positive-electrode material also suppresses elution of the manganese to the electrolytic solution by elevated-temperature preservation.
[0005] Li1-z which is the main constituent of a positive active material In [Mn2-x-y Mx Liy O4], M is elements other than Mn and Li, and its element which can be replaced by Mn is desirable. For example, Be, B, C, Si, P, Sc, Cu, Zn, Ga, germanium, As, Se, Sr, Mo, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, W.Pb, Bi, Co, Fe, Cr, nickel, Ti, Zr, Nb, Y, aluminum, Na, K, Mg, calcium, Cs, La, Ce, Nd, Sm, Eu, Tb, etc. are mentioned. Also in these, since the effect of Cr, calcium, In, Tb, and Mg was remarkable, they are the most desirable. Here, x and y which show the amount of substitution of Mn are $0<x+y<=1$. however, the thing replaced in $0<x+y<=0.2$ in order that z which shows the amount of lithiums usable in reversible may decrease, if amount x+y of substitution of Mn is increased -- good -- better Although z which shows the amount of lithiums usable in reversible changes also with amounts of substitution of Mn, it is $-1<=z<=1$.
[0006] Li1-z which is the main constituent of a positive active material The method of adding the element beforehand replaced by the baking raw material in [Mn2-x-y Mx Liy O4], when a lithium and a different-species element replace a part of Mn, and LiMn 2O4 Although the way the ion exchange etc. replaces a different-species element etc. is mentioned after calcinating, it is not limited to these.
[0007] The spacing (d002) especially by the X-ray diffraction method is 3.354 to 3.369 A, and since high capacity is obtained, the carbon particle whose size (Lc) of the crystal of C shaft orientations is 200A or more is [that the carbon material used for a negative-electrode active material should just be a carbon material which emits / occlusion and / a lithium] desirable.
[0008] As for the positive electrode used for this invention, and a negative-electrode active material, it is desirable that it is 100 micrometers or less of average grain size. When acquiring a predetermined configuration, a grinder and a classifier are used in order to obtain fine particles. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a planet ball mill, a jet mill, a counter jet mill, a revolution air current type jet mill, a thermal plasma, a screen, etc. are used. At the time of trituration, wet grinding which made organic solvents, such as water or a hexane, live together can also be used. As the classification method, there is especially no limitation and a screen, a pneumatic elutriation machine, etc. are used if needed in dry type and wet.
[0009] As a negative-electrode material which can be combined and can be used for this invention, the organic compound containing lithiums, such as a lithium metal, a lithium alloy, etc. and a chalcogen compound, a methyl lithium, etc. is mentioned. Moreover, it is also possible by using together the organic compound containing a lithium metal, a lithium alloy, and a lithium to insert a lithium in the carbon material used for this invention beforehand.

[0010] the case where the positive electrode of this invention and a negative-electrode active material are used -- an electrode -- an electric conduction agent, a binder, a filler, etc. can be added as a mixture If it is the electronic-conduction nature material which does not have a bad influence on a cell performance as an electric conduction agent, it is good anything. Usually, conductive material, such as natural graphites (a flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon whisker, carbon fiber metallurgy group powder (copper, nickel, aluminum, silver, gold, etc.), a metal fiber, and a conductive ceramic material, can be included as one sort or those mixture. In these, combined use of acetylene black and KETCHIEN black is desirable. The addition has 1 - 50 desirable % of the weight, and its 2 - 30 % of the weight is especially desirable.

[0011] When using the positive electrode of this invention, and a negative-electrode active material, the thing of the fine particles for which it is things other than the main active material, and a surface-layer portion is embellished at least is also possible. For example, applying technology, such as plating, sintering, a mechano fusion, and vacuum evaporationo, and carrying out the coat of the ion conductivity good matter, such as good matter of electronic-conduction nature, such as gold, silver, carbon, nickel, and copper, and a lithium carbonate, boron glass, a solid electrolyte, is mentioned.

[0012] As a binder, thermoplastics, such as a tetrafluoroethylene, a polyvinylidene fluoride, polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), sulfonation EPDM, styrene butadiene rubber (SBR), a fluororubber, and a carboxymethyl cellulose, the polymer which has rubber elasticity, polysaccharide, etc. can usually be used as one sort or two sorts or more of mixture. Moreover, as for a lithium and the binder which has the functional group which reacts, it is desirable like polysaccharide to methylate, for example and to make the functional group deactivate. As the addition, 1 - 50 % of the weight is desirable, and 2 - 30 % of the weight is especially desirable.

[0013] If it is the material which does not have a bad influence on a cell performance as a filler, it is good anything. Usually, olefin system polymer, such as polypropylene and polyethylene, Aerosil, a zeolite, glass, carbon, etc. are used. The addition of a filler has 0 - 30 desirable % of the weight.

[0014] If it is the electronic-conduction object which does not do a bad influence in the constituted cell as a charge collector of an electrode active material, it is good anything. For example, as a charge collector for positive electrodes, besides aluminum, titanium, stainless steel, nickel, a baked carbon, a conductive polymer, electrically conductive glass, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as aluminum and copper, with carbon, nickel, titanium, silver, etc. can be used. As a charge collector for negative electrodes, besides copper, stainless steel, nickel, aluminum, titanium, a baked carbon, a conductive polymer, electrically conductive glass, an aluminum-Cd alloy, etc., it is the purpose of an adhesive property, conductivity, and oxidation-resistant improvement, and what processed front faces, such as copper, with carbon, nickel, titanium, silver, etc. can be used. About such material, it is also possible to oxidize a front face. About these configurations, the shape of the shape of others and a film and a sheet, the letter of a network, punch or the thing by which expanded one was carried out, a lath object, a porosity object, a foam, the organizer of a fiber group, etc. are used. [shape / of foil] Although especially limitation is thin, a 1-500-micrometer thing is used.

[0015] It is Li1-z to the main constituent of a positive active material. When using [Mn2-x-y Mx Liy O4], it is also possible to add other positive active materials. for example, MnO2, MoO3, V2 O5, Lix CoO2, and Lix NiO2 etc. -- a metallic oxide, and TiS2, MoS2 and NbSe3 etc. -- various kinds of matter in which absorption/emission is possible can be used for alkali-metal ion, such as intercalated graphite, such as a metal chalcogen ghost, the poly acene, poly para-phenylene, polypyrrole, the poly aniline, and disulfide, and a conductive polymer, and an anion Applying and carrying out the coat of the technology, such as electrolytic polymerization, plating, sintering, a mechano fusion, and vacuum evaporationo, as the addition method besides only mixing is mentioned.

[0016] Moreover, it is desirable to be able to use the organic electrolytic solution, a solid polymer electrolyte, an inorganic solid electrolyte, fused salt, etc., for example, and to use the organic electrolytic solution also in this as an electrolyte. As an organic solvent of this organic electrolytic solution, propylene carbonate, ethylene carbonate, Butylene carbonate, diethyl carbonate, dimethyl carbonate, Ester, such as methylethyl carbonate and gamma-butyrolactone Substitution tetrahydrofurans, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, A dioxolane, diethylether, dimethoxyethane, diethoxy ethane, Ether, such as methoxyethoxy ethane, dimethyl sulfoxide, a sulfolane, a methyl sulfolane, an acetonitrile, methyl formate, methyl acetate, N-methyl pyrrolidone, a dimethyl formamide, etc. are mentioned, and these can be used as independent or a mixed solvent. moreover -- as a supporting-electrolyte salt -- LiClO4, LiPF6, LiBF4, LiAsF6, LiCF3 SO3, LiN (CF3 SO2)2, LiN (C2 F5 SO2)2, and LiN (CF3 SO2) (C4 F9 SO2)2 etc. -- it is mentioned On the other hand, what melted the above supporting-electrolyte salts as a solid polymer electrolyte into polymer, such as a polyethylene oxide, the bridge formation object and poly force FAZEN, and its bridge formation object, can be used. Furthermore, inorganic solid electrolytes, such as Li3 N and LiI, are also usable. That is, what is necessary is just nonaqueous electrolyte of

lithium ion conductivity.

[0017] As separator, the transmittance of ion is excellent and an insulating thin film with a mechanical strength can be used. The sheet built with the polymer of olefin systems, such as organic-solvent-proof nature, hydrophobic shell polypropylene, and polyethylene, the glass fiber, the polyvinylidene fluoride, the polytetrafluoroethylene, etc., a micropore film, a nonwoven fabric, and cloth are used. The aperture of separator is a thing of the range generally used for a cell, for example, is 0.01-10 micrometers. Moreover, the same is said of the thickness, and it is the thing of the range generally used for a cell, for example, is 5-300 micrometers.

[0018] As a reason a charge-and-discharge property, especially whose cycle property improve, although it is not necessarily clear, it is considered as follows. Generally, in the interior of a cell, the various impurities which do not participate in the charge and discharge of a cell are included in many cases. For example, LiPF6 When using for an electrolyte, the salt itself can carry in an impurity or it is possible to produce HF (fluoric acid) reacting with the water of the ultralow volume contained in the interior of a cell, or a solvent. Although an ion conductivity high coat like a lithium carbonate is formed between the electrolytic solution and a carbon material on a carbon-material front face in the case of lithium occlusion, if an acid like fluoric acid exists after the time of this coat formation, or formation, an ion conductivity low lithium halide will be produced. The lithium halide produced in the interface of a carbon material and the electrolytic solution bars occlusion discharge of a lithium, as a result, increases the interfacial resistance of a negative electrode, and is considered to be one of the causes which service capacity reduces. Then, I thought that this problem would be solvable by reducing the amount of the fluoric acid which exists in the interior of a cell. That is, by the manganic acid lithium which is a positive active material thinking that decomposition will be promoted in catalyst, and using the manganic acid lithium which has the Spinel structure which replaced some manganese by elements other than a lithium and manganese, although it thinks that it is generated by the reaction of an electrolyte and water, this fluoric acid is ****, when the fluoric acid which drops the catalyst-activity exerted on decomposition etc. and is produced by the decomposition reaction of water and an electrolyte is reduced. Furthermore, this catalyst-activity is LiMn 2O4 which has Spinel structure. Gamma-MnO 2 which is the matter after charge By being the highest and replacing some manganese by elements other than a lithium and manganese This gamma-MnO 2 By using the manganic acid lithium which has the Spinel structure which suppressed generation, thought that catalytic activity could be reduced and replaced some manganese by elements other than a lithium and manganese Since interfacial-resistance increase of the carbon material of a negative electrode was suppressed and the cycle property improved, it resulted in this invention. Moreover, it turns out that its stability of an active material own [hot] improves catalytic activity not only reduced the manganic acid lithium which has the Spinel structure which replaced a part of this manganese by elements other than a lithium and manganese, but, and a hot cycle property also improves.

[Translation done.]

EXAMPLE

[Example] Hereafter, this invention is explained based on an example.
[0020] (Example 1) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the calcium-acetate monohydrate were mixed so that Li and the ratio of Mn and calcium might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of calcium was observed by energy-dispersion type electron probe microanalysis (EPMA), calcium was distributed all over the manganic acid lithium. Let this powder be Powder A.
[0021] (Example 2) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the chromium acetate (III) were mixed so that the ratio of Li, and Mn and Cr might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of chromium was observed by EPMA, chromium was distributed all over the manganic acid lithium. Let this powder be Powder B.
[0022] (Example 3) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and the acetic-acid indium (III) hydrate were mixed so that the ratio of Li, and Mn and In might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of an indium was observed by EPMA, the indium was distributed all over the manganic acid lithium. Let this powder be Powder C.
[0023] (Example 4) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and acetic-acid terbium (III) 4 hydrate were mixed so that Li and the ratio of Mn and Tb might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of a terbium was observed by EPMA, the terbium was distributed all over the manganic acid lithium. Let this powder be Powder D.
[0024] (Example 5) The acetic-acid lithium dihydrate, manganese acetate (II)4 hydrate, and magnesium-acetate (II) 4 hydrate were mixed so that Li and the ratio of Mn and Mg might be set to 1.10:1.95:0.05, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Next, when the distributed state of a chromium element was observed by EPMA, magnesium was distributed all over the manganic acid lithium. Let this powder be Powder E.
[0025] (Example 6) The coin type nonaqueous electrolyte cell shown in drawing 1 as follows was made as an experiment, using the powder A, B, C, D, and E obtained in the above-mentioned example 1 as a positive active material. The positive electrode 1 mixed Powder A - Powder E, acetylene black, and polytetrafluoroethylene powder by the weight ratio 85:10:5, added toluene, and kneaded it enough. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, and

dried at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. As a negative-electrode active material, it is an artificial graphite (the size (Lc) of the crystal of the spacing (d002) by 6 micrometers of mean particle diameters and the X-ray diffraction method of C shaft orientations by 3.37A mixed 550A and polytetrafluoroethylene powder by the weight ratio 95:5, added toluene, and kneaded enough.). This was fabricated with a thickness of 0.1mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, it dried at 200 degrees C under reduced pressure for 15 hours, and the negative electrode 2 was obtained The negative electrode 2 was stuck by pressure and used for the negative-electrode can 5 to which the negative-electrode charge collector 7 was attached. It is LiPF6 to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porous membrane made from polypropylene was used for separator 3 using the electrolytic solution which carried out 1 mol/l dissolution. The coin type lithium cell with a diameter [of 20mm] and a thickness of 1.6mm was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and separator. Let the cells using this powder A-E be a cell (A) - a cell (E), respectively.

[0026] (Example of comparison) The acetic-acid lithium dihydrate and manganese acetate (II)4 hydrate were mixed so that the ratio of Li and Mn might be set to 1.10:2.00, and this was dissolved in the acetic acid. It agitated applying heat, the acetic acid was evaporated from the solution which dissolved completely, and the mixed salt was obtained. Temporary baking of this mixed salt was carried out at 500 degrees C, and it calcinated at 850 degrees C among air. As a result of grinding the obtained baking object and performing this XRD measurement, it turns out that the manganic acid lithium which has Spinel structure is obtained. Let this powder be Powder C. Instead of Powder A, Powder F was used and the cell was produced like the example 3 except it. Let the obtained cell be a comparison cell (F).

[0027] These cells (A) The charge and discharge test was performed using - (E) and the comparison cell (F). Charge final voltage was set to 4.2V, the discharge final voltage was set to 3.0V, and 1mA and the test temperature performed constant-current charge and discharge for the charge and discharge current at 20 degrees C and 40 degrees C. The result of the service capacity of obtained 5 cycle eye was shown in Table 1. Moreover, the number of cycles at the time of service capacity falling to 60% of the first stage as a cycle life was measured.

[0028]

[Table 1]

電池	２０℃での放電容量（mAh）	サイクル寿命（サイクル数）	４０℃での放電容量（mAh）	サイクル寿命（サイクル数）
電池A	１６	２８５	１７	１４５
電池B	１６	２６５	１７	１４０
電池C	１６	３００	１７	１６０
電池D	１６	２６５	１７	１４０
電池E	１６	２７５	１７	１４５
比較電池F	１７	８０	１４	１０

[0029] Although the cell (A) - cell (E), and comparison cell (F) using Powder A - Powder E were compared and early service capacity did not change, a cycle life is good and a bird clapper is known. Moreover, in the elevated temperature of 40 degrees C, it turns out that early service capacity increases and a cycle life also improves. That is, there is little electrolytic disassembly by using the positive active material of this invention, and since generation of fluoric acid is suppressed by this, in the surface lining generated on a carbon front face, it is possible [it] that the coat of the component like the low lithium carbonate of comparatively resistance or a lithium oxide in which not the high lithium fluoride of the resistance generated under existence of fluoric acid but a fluorine does not participate is formed, interfacial-resistance increase is suppressed, and a cycle property improves. moreover, since the 40-degree

C hot cycle property is also excellent, not only in electrolytic disassembly In the above-mentioned example which can consider that elution of the manganese to the own electrolytic solution of a positive active material is also suppressed, and capacity deterioration of an active material is also suppressed To the main constituent in a positive active material, Li [Mn1.95calcium0.05Li 0.10O4], Li [Mn1.95Cr0.05Li 0.10O4] and Li [Mn1.95In0.05Li 0.10O4], Li [Mn1.95Tb0.05Li 0.10O4] Although Li [Mn1.95Mg0.05Li 0.10O4] was mentioned about the lithium secondary battery using the artificial graphite as a negative-electrode material, the same effect was checked about other substitution elements and negative-electrode material. In addition, this invention is not limited to the start raw material, the manufacture method, a positive electrode, a negative electrode, an electrolyte, separator, a cell configuration, etc. of the active material indicated by the above-mentioned example.

[Translation done.]

DESCRIPTION OF DRAWINGS

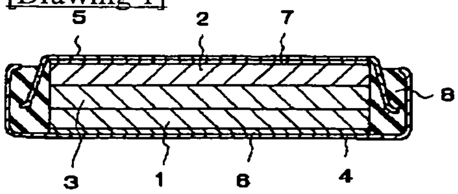
[Brief Description of the Drawings]
[Drawing 1] It is the cross section of the coin type nonaqueous electrolyte cell concerning the example of this invention.
[Description of Notations]
1 Positive Electrode
2 Negative Electrode
3 Separator
4 Positive-Electrode Can
5 Negative-Electrode Can
6 Positive-Electrode Charge Collector
7 Negative-Electrode Charge Collector

[Translation done.]

* NOTICES *

DRAWINGS

[Drawing 1]



[Translation done.]